

Lifetimes, transition probabilities, and level energies in Fe I

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We use time-resolved laser-induced fluorescence to measure the lifetime of 186 Fe I levels with energies between 25 900 and 60 758 cm^{-1} . Measured emission branching fractions for these levels yield transition probabilities for 1174 transitions in the range 225–2666 nm. We find another 640 Fe I transition probabilities by interpolating level populations in the inductively coupled plasma spectral source. We demonstrate the reliability of the interpolation method by comparing our transition probabilities with absorption oscillator strengths measured by the Oxford group [Blackwell *et al.*, *Mon. Not. R. Astron. Soc.* **201**, 595–602 (1982)]. We derive precise Fe I level energies to support the automated method that is used to identify transitions in our spectra.

1. INTRODUCTION

We recently demonstrated with Mo I an automated method for extracting a large number of atomic transition probabilities of modest precision from Fourier-transform spectra.¹ In the present paper we apply this method to a more important and better-known atom, Fe I, for which accurate *gf* values already exist against which we can test the results of our method. The method requires the radiative lifetime of many atomic levels—the more the better—with excitation energies distributed over the maximum possible range; in Section 2 we report the measurement by laser fluorescence of the lifetime of 186 Fe I levels between 25 900 and 60 758 cm^{-1} .

In Section 3 we report the automated measurement of emission branching fractions for the decay of these levels and determine transition probabilities for the decay channels. In Section 4 we use the transition probabilities to investigate the population of excited Fe I levels in the inductively coupled plasma (ICP) source and show that one can interpolate between levels of known lifetimes, and hence of known populations, to find the population of new levels of unknown lifetime. Once the population of a level is known, the transition probability can be found for every measurable transition by which the level decays. The two methods combined yield 1814 transition probabilities. We publish in this paper only a sample of the stronger lines; as in the case of Mo I, those who need the complete results may obtain them on request in machine-readable form.

To establish the soundness of our population method and validate the uncertainty estimates that we assign, in Section 5 we compare Fe I transition probabilities measured by the lifetime and the population methods with the precise absorption oscillator strengths measured by Blackwell *et al.*² With the reliability of our results confirmed,

we proceed to use our values to test the precision of two other collections of Fe I transition probabilities: the 1985 National Institute of Standards and Technology (NIST) compilation³ (2092 lines) and the semiempirical values of Kurucz⁴ ($\sim 10^6$ lines). To support the automated line-identification process, in Section 6 we present improved Fe I level energies determined from our spectra, and we compare our level energies with those in the NIST *Atomic Energy Levels*⁵ (AEL).

2. LEVEL LIFETIMES

Radiative lifetimes for 186 levels of Fe I were measured with time-resolved laser-induced fluorescence on a slow Fe atomic beam. This approach has proved highly reliable for measurements on neutral and singly ionized atoms.⁶ Selective laser excitation eliminates the cascading problem that plagues beam-foil time-of-flight measurements. The beam environment eliminates errors that are due to radiation trapping and collisional quenching.

Figure 1 is a schematic of the experiment. The atomic or ionic beam source is based on a low-pressure large-bore hollow-cathode discharge. This versatile sputter source produces intense atomic or ionic beams of any metallic element. The hollow cathode is used to form uncollimated atomic or ionic beams by sealing one end of the cathode except for a 1.0-mm-diameter opening, flared outward at 45°. The hollow cathode and the scattering chamber are at ground potential. Ar, the sputtering gas, flows continuously into the hollow-cathode discharge. The scattering chamber is sealed from the hollow-cathode discharge, except for the nozzle, and is maintained at a much lower pressure than the discharge by a 10-cm diffusion pump. The Ar pressure in the discharge is typically 0.4 Torr, while the scattering chamber pressure is 10^{-4} Torr. The hollow-cathode discharge is operated with dc currents of

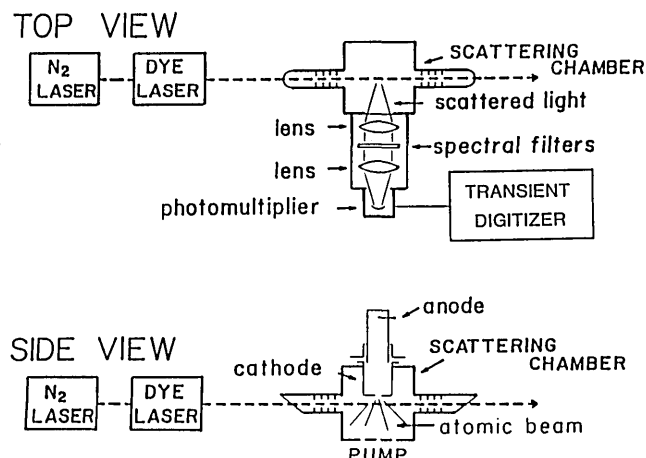


Fig. 1. Schematic diagram of the laser fluorescence apparatus.

20–200 mA and with 5- μ s pulses as large as 25 A. When operated in a pulse mode the discharge current is maintained at 50 mA between pulses by the dc supply. A more detailed description of the source, including a drawing showing dimensions and materials, has been published.⁷

The atomic beam is crossed by a pulsed dye-laser beam 1.0 cm from the nozzle. The dye laser, pumped by a pulsed N₂ laser, produces an optical pulse of 3-ns duration (FWHM) with a 0.2-cm⁻¹ bandwidth and a peak power of up to 40 kW. Potassium dihydrogen phosphate (KDP) and β -barium borate (BBO) crystal frequency doublers extend the dye laser tuning range to 205 nm in the UV. The fluorescence is detected along an axis orthogonal to the atomic beam and laser beam. In order to minimize scattered light, several sets of light baffles are arranged along the laser-beam axis inside the Brewster windows that pass the laser beam into and out of the scattering chamber. Two independently tuned dye lasers were used to excite six of the high-lying even-parity levels by two-step laser excitation.

Two lenses composing an $f/1$ system with unity magnification are used to collect the laser-induced fluorescence. The fluorescent light is approximately collimated between the two lenses. Interference filters or dye filters may be inserted between the lenses. Occasionally, branching ratios are favorable for observing fluorescence at a wavelength that is much different from the laser wavelength. Filters are used to block all scattered laser light and to isolate the laser-induced fluorescence whenever possible. Repopulation by radiative cascade from higher-lying levels is not a problem because of the highly selective laser excitation. Filters are used to block emission from lower-lying levels, which are populated by radiative cascade. High-lying even-parity levels are prone to produce cascade fluorescence from lower odd-parity levels.

The detection system is composed of a photomultiplier, a delay cable, and either a boxcar averager or a transient digitizer. The bias resistors of the 1P28A photomultiplier are bypassed with capacitors in order to ensure good linearity at large peak currents; small damping resistors are included to reduce ringing. All components are wired for low inductance and fast response. The 0.1-ns rise-time delay cable is necessary for synchronization of electronic components when the boxcar averager is used. The window width of the PAR-163/162 boxcar averager is

75 ps. Most of the 6070 fluorescence decay curves for this study were logged with a Tektronix 7912AD transient digitizer, shown in Fig. 1, since its data collection rate is a hundred times that of the boxcar. The digitizer has an analog bandwidth of 0.5 GHz and a sampling rate of 200 GHz. We often compared the two data-logging systems in order to test for small systematic errors. Measuring well-known He I and Be I lifetimes tests the accuracy of the experiment and confirms that lifetimes as short as 2 ns can be accurately measured.⁸ A trigger generator provides an adjustable delay between the current pulse to the hollow cathode and the laser pulse. Pulsing the atomic beam source has two advantages: It produces a much higher flux of atoms, especially in high metastable levels (while still maintaining low average discharge current), and it permits extensive studies of potential error in very long (~ 2 - μ s) lifetimes that arises from atoms' escaping from the observation region before radiating.⁹ Error due to atoms' escaping from the observation region before radiating is negligible in this Fe I experiment.

We routinely use more than one transition for laser excitation of a level. This redundancy provides a check that the chosen transitions have been correctly classified, are correctly identified in the experiment, and are unblended. Typically these independent measurements agree to a few percent. One of the most interesting discoveries during this investigation is that long-lived ($\geq 10^{-4}$ s) odd-parity levels have useful populations in the atomic beam. All but six of the lifetimes for high-lying even-parity levels were measured with single-step laser excitation. Two-step excitation, which was necessary for the six levels from the e^5H and e^3H terms, confirms the classification of lines connected to these levels, because the fluorescence from these levels is extinguished when either laser beam is interrupted.

The dynamic range of this experiment extends from 2-ns lifetimes, where it is limited by the electronic bandwidth of the detection apparatus, to 2- μ s lifetimes, where it is limited by atoms' escaping from the observation region before radiating. Other possible systematic errors from radiation trapping, collisional quenching, or Zeeman quantum beats are unimportant. Tests for radiation trapping are routinely performed by variation of the atomic beam intensity. Many such tests on strong resonance transitions were performed, and radiation trapping of metal atom transitions was not detected. Collisional quenching is not a problem because of the low scattering chamber pressure (10^{-4} Torr of Ar). The absence of collisional quenching is confirmed by variation of the scattering chamber pressure when long lifetimes are measured. Zeeman quantum beats are avoided by measurement of short (< 300 -ns) lifetimes in zero magnetic field (< 20 mG) and long (> 300 -ns) lifetimes in a high (30 G) field. We claim a total uncertainty that is the greater of $\pm 5\%$ or ± 0.2 ns in our lifetime measurements. This uncertainty includes both systematic and random error. Our lifetime measurements and the transitions used for laser excitation are listed in Table 1.

A comparison of our measurements with those of previous investigations, especially laser-induced fluorescence measurements, provides convincing evidence that our total uncertainty is a realistic estimate of both systematic and random error. In Table 1 we list (on the line below our

Table 1. Radiative Lifetime of Fe I Levels*

Level	Energy (cm ⁻¹)	Transitions (nm)	τ (ns)				
				$z^3G_5^o$	35379.204	427.18	10.2
				$z^5G_3^o$	35611.621	433.70, 441.51	10.2
							10.3(6) ^b
$z^5D_4^o$	25899.986	385.99, 539.71	78.2	$z^3G_4^o$	35767.560	420.20, 430.79	10.8
		89.0(4.8) ^a , 81.4(5.0) ^b , 78.5(2.0) ^c		$z^5G_2^o$	35856.397	436.79	9.9
$z^5D_3^o$	26140.177	388.63, 532.80	81.1	$z^3G_3^o$	36079.368	425.08, 432.58	11.7
		87.2(4.8) ^a , 83.5(5.0) ^b		$y^3F_4^o$	36686.172	404.58, 414.39	9.6
$z^5D_2^o$	26339.694	385.64, 537.15	84.5				9.11(16) ^e
		94.7(5.3) ^a , 82.3(5.0) ^b		$y^5P_3^o$	36766.963	403.26, 520.23	5.7
$z^5D_1^o$	26479.376	387.86, 540.58	86.3	$y^5P_2^o$	37157.561	406.45, 509.87	6.0
		91.2(5.0) ^a , 83.5(5.0) ^b		$y^3F_3^o$	37162.743	406.36, 413.21	9.5
$z^5D_0^o$	26550.474	389.57, 543.45	88.5				9.06(13) ^e
		88.6(5.0) ^a , 85.6(5.0) ^b		$y^5P_1^o$	37409.549	507.92, 513.15	6.2
$z^5F_5^o$	26874.546	501.21, 512.74	60.5	$y^3F_2^o$	37521.157	400.52, 407.17	9.6
		62.4(4.2) ^b , 61.0(1.0) ^c					9.06(16) ^e
$z^5F_4^o$	27166.816	505.16, 514.29	63.6	$y^3D_3^o$	38175.348	381.58, 390.30	7.1
		63.7(4.0) ^b		$y^3D_2^o$	38678.034	382.78, 388.85	7.1
$z^5F_3^o$	27394.687	499.41, 508.33	66.3	$y^3D_1^o$	38995.731	384.11	7.2
		65.1(4.0) ^b		$x^5D_4^o$	39625.799	452.86	2.6
$z^5F_2^o$	27559.580	504.11, 515.19	67.9	$x^5D_3^o$	39969.848	449.46	2.6
$z^5F_1^o$	27666.344	507.97, 512.37	68.8	$y^7P_2^o$	40052.018	255.26, 444.28	444
		64.6(4.0) ^b		$y^7P_3^o$	40207.090	248.64, 251.24	146
$z^3D_3^o$	31322.610	319.17, 532.85	254	$x^5D_2^o$	40231.332	448.23	2.6
$z^3D_2^o$	31686.349	319.70, 534.10	245	$x^5F_5^o$	40257.307	248.33	2.0
$z^3D_1^o$	31937.323	322.91, 527.04	237	$x^5D_1^o$	40404.513	444.77	2.6
$y^5D_4^o$	33095.937	382.04, 388.71	5.9	$y^7P_4^o$	40421.938	247.32	309
$y^5D_3^o$	33507.119	382.59, 387.80	5.7	$x^5D_0^o$	40491.279	443.06	2.6
		6.1(5) ^d		$x^5F_4^o$	40594.427	248.81	2.0
$y^5F_5^o$	33695.394	460.29	7.9	$x^5F_3^o$	40842.149	247.29	2.0
		8.16(30) ^a		$z^5S_2^o$	40894.986	248.74, 428.24	36.9
$y^5D_2^o$	33801.568	383.42, 387.25	6.5	$x^5F_2^o$	41018.046	247.98	2.0
$z^3P_2^o$	33946.929	385.08, 387.60	38.3	$x^5F_1^o$	41130.594	248.42, 248.98	2.0
		37.0(2.2) ^b , 38.6(2.0) ^d		$x^5P_3^o$	42532.736	237.36, 239.00	46.6
$y^5D_1^o$	34017.099	384.04, 386.55	5.8	$y^5G_6^o$	42784.350	278.81	16.9
		6.1(2) ^d		$e^7D_5^o$	42815.851	426.05	8.3
$y^5F_4^o$	34039.512	453.12, 465.45	7.7	$x^5P_2^o$	42859.773	237.14, 238.18	30.4
		8.29(30) ^a		$y^5G_5^o$	42911.911	277.82, 281.33	23.1
$y^5D_0^o$	34121.597	385.00	5.8	$z^5H_5^o$	42991.693	280.70	72.1
		5.9(2) ^d		$y^5G_4^o$	43022.979	280.45, 283.24	28.6
$y^5F_3^o$	34328.748	459.27, 468.03	7.7	$x^5P_1^o$	43079.019	237.45	93.0
		7.92(25) ^a		$z^5H_4^o$	43108.913	279.78, 282.56	55.2
$z^3P_1^o$	34362.869	379.01, 381.45	99.6	$y^5G_3^o$	43137.483	282.33	20.5
		94.1(5.5) ^b , 112(11) ^d		$e^7D_4^o$	43163.321	423.59, 427.12	8.5
$y^5F_2^o$	34547.206	454.70, 463.29	7.7	$y^5G_2^o$	43210.020	281.75, 283.81	20.8
		8.00(30) ^a		$z^5H_3^o$	43325.960	282.88	391
$z^3P_0^o$	34555.592	296.94, 378.67	112	$e^7D_3^o$	43434.624	418.78, 425.01	8.4
		108.0(7.0) ^b , 111.5(5.0) ^d		$w^5D_4^o$	43499.503	273.36, 385.26	7.4
$y^5F_1^o$	34692.143	460.20	7.8	$e^7D_2^o$	43633.529	418.70, 423.36	8.4
		7.86(25) ^a		$e^7D_1^o$	43763.977	419.14, 421.03	8.4
$z^5G_5^o$	34782.417	438.36	11.6	$w^5D_3^o$	43922.665	273.55, 381.63	8.5
		11.7(7) ^b		$^5D_4^o$	44022.521	229.25, 272.80	95.9
$z^5G_4^o$	35257.321	429.41, 440.48	10.8	$^5D_3^o$	44166.200	230.01, 274.36	68.3
		11.2(7) ^b		$w^5D_2^o$	44183.622	274.23, 316.14	8.9
				$^5F_5^o$	44243.682	225.95, 267.91	39.0
				$^5F_4^o$	44285.451	229.38, 230.36	54.0
				$^5F_1^o$	44378.338	229.87, 230.34	41.7

(continued overleaf)

Table 1. Continued

Level	Energy (cm ⁻¹)	Transitions (nm)	τ (ns)				
w ⁵ D ₁ ^o	44411.153	274.45, 275.73	10.5	f ⁷ D ₁	51048.100	321.08	7.0
⁵ F ₄ ^o	44415.069	227.21, 269.91	41.2	e ⁷ F ₃	51148.857	316.50, 318.46, 320.05	8.3
w ⁵ D ₀ ^o	44458.930	229.44, 275.37	11.5	e ⁵ S ₂	51148.905	321.15	9.6
y ⁵ S ₂ ^o	44511.807	226.71, 271.78	13.6	e ⁷ F ₄	51192.269	318.02	6.5
⁵ F ₃ ^o	44551.333	227.99, 268.92	41.6	e ⁷ F ₁	51207.993	320.54	5.9
⁵ D ₂ ^o	44664.074	228.37, 270.66	31.7	e ⁵ G ₃	51219.012	315.80, 319.33	9.5
⁵ D ₁ ^o	44760.741	226.91, 271.84	21.4	e ⁷ G ₅	51228.548	315.70	7.8
⁵ D ₀ ^o	44826.880	227.52, 272.61	16.3	e ⁷ F ₂	51331.050	318.19	7.4
x ³ D ₃ ^o	45220.674	223.12, 264.16	23.0	e ⁷ G ₄	51334.905	316.59	7.5
x ³ D ₂ ^o	45281.828	225.19, 388.55	21.3	e ⁵ G ₂	51370.141	316.23, 318.88	10.3
y ³ G ₅ ^o	45294.841	260.57, 385.92	55.7	e ⁷ G ₃	51460.514	315.33, 316.89	6.7
y ³ G ₄ ^o	45428.397	387.38, 389.90	64.0	f ⁵ F ₄	51461.669	315.32	12.7
x ³ D ₁ ^o	45551.760	306.82, 384.52	19.8	e ⁷ G ₂	51539.718	317.17	6.7
y ³ G ₃ ^o	45562.970	266.04, 306.71	67.2	e ⁷ S ₃	51570.094	314.25, 315.79	7.3
x ⁵ G ₆ ^o	45608.358	258.45	31.4	f ⁵ F ₃	51604.100	315.45	14.8
x ⁵ G ₅ ^o	45726.126	257.67, 260.68	28.1	w ³ H ₆ ^o	52431.438	302.56, 379.75	8.9
x ⁵ G ₄ ^o	45833.219	262.35	26.8	y ³ I ₆ ^o	52513.552	303.93	11.2
x ⁵ G ₃ ^o	45913.498	261.80, 263.58	26.4	w ³ H ₅ ^o	52613.083	303.01, 380.67	9.1
x ⁵ G ₂ ^o	45964.953	263.22, 264.40	26.8	y ³ I ₇ ^o	52654.983	300.53	10.2
z ³ I ₉ ^o	45978.002	376.01	191	w ³ H ₄ ^o	52768.736	303.12, 382.43	9.3
z ³ I ₈ ^o	46026.965	378.60	200	y ³ I ₅ ^o	52898.990	300.41	10.7
z ³ I ₅ ^o	46135.812	379.43	211	e ⁵ H ₆	53352.980	538.34 + 438.36	12.8
z ³ H ₆ ^o	46982.315	249.59, 395.67	43.3			12.8(8) ^b	
z ³ H ₅ ^o	47008.366	252.25, 399.74	35.9	g ⁷ D ₅	53800.856	290.19, 320.93	22.7
z ³ H ₄ ^o	47106.479	251.63, 284.57, 402.19	36.5	e ³ H ₆	53840.614	541.52 + 427.18	12.8
w ⁵ G ₆ ^o	47363.371	389.79	60.0	e ⁵ H ₅	53874.251	537.00 + 440.48	12.9
w ⁵ G ₅ ^o	47420.224	246.89, 249.65	20.2			13.4(9) ^b	
w ⁵ G ₄ ^o	47590.042	248.60, 250.79	35.5	t ³ G ₅ ^o	53983.294	309.82	12.0
w ⁵ G ₃ ^o	47693.236	251.77, 389.08	41.0	g ⁷ D ₄	54124.735	289.25, 290.89	24.3
x ³ G ₄ ^o	47812.114	244.52, 283.59	44.8	e ⁵ H ₄	54237.156	536.75 + 441.51	12.9
w ⁵ G ₂ ^o	47831.149	251.96, 390.79	34.2	t ³ G ₄ ^o	54237.409	288.80, 307.40	10.9
x ³ G ₃ ^o	47834.215	249.26, 250.88	102	e ³ H ₅	54266.706	540.42 + 430.79	13.0
x ³ G ₅ ^o	47834.547	244.39, 247.10	43.6	e ³ H ₄	54555.413	541.09 + 432.58	13.7
⁵ H ₅ ^o	48231.275	242.04, 377.03	175	t ³ G ₃ ^o	54600.345	306.65, 309.02	10.1
⁵ H ₄ ^o	48361.875	279.24, 379.22	139	g ⁷ D ₂	54611.711	286.82, 318.18	22.8
⁵ H ₃ ^o	48475.680	281.55, 364.37, 381.19	130	g ⁷ D ₁	54747.608	286.98, 317.34	23.0
y ³ H ₆ ^o	49434.159	389.75	11.5	³ H ₄ ^o	55446.004	280.36, 301.15	17.0
v ³ G ₅ ^o	49460.896	266.70, 389.34	11.4	³ H ₆ ^o	55489.734	276.93, 296.00	11.1
y ³ H ₅ ^o	49604.422	265.68, 387.17	11.6	³ H ₅ ^o	55525.555	278.43, 295.69	9.0
y ³ G ₄ ^o	49627.878	269.70, 391.91	11.3	u ³ H ₆ ^o	56333.955	270.60, 288.78	19.8
y ³ H ₄ ^o	49726.985	268.98, 390.39	11.3	u ³ H ₅ ^o	56382.656	271.94, 290.75	12.6
v ³ G ₃ ^o	49850.584	271.05, 391.86	11.6	u ³ H ₄ ^o	56423.276	271.64, 272.88	10.4
e ⁷ F ₆	50342.127	322.58	5.6	u ³ F ₄ ^o	56592.695	271.63, 278.07, 304.7	9.9
f ⁷ D ₅	50377.905	324.42	5.7	u ³ F ₃ ^o	56783.316	278.40, 306.05	11.4
e ⁵ G ₆	50522.940	320.71	13.0	x ³ I ₇ ^o	57027.505	265.62	17.2
		13.0(8) ^b , 13.0(7) ^f		x ³ I ₆ ^o	57070.165	266.95	17.4
e ⁵ G ₅	50703.865	318.86, 321.02	11.5	x ³ I ₅ ^o	57104.205	307.32, 328.03	17.2
		11.7(7) ^b		t ³ F ₄ ^o	57550.005	270.86, 278.98	9.2
f ⁷ D ₄	50807.993	321.96	6.2	t ³ F ₃ ^o	57641.005	254.62, 270.19	7.9
e ⁷ F ₅	50833.432	317.54	6.7	t ³ F ₂ ^o	57708.742	271.41, 272.62	8.9
f ⁷ D ₃	50861.816	321.40	7.4	³ I ₇ ^o	58792.247	253.72	2.7
e ⁷ G ₆	50967.826	316.20	6.5	³ I ₆ ^o	58946.730	254.21	2.0
e ⁵ G ₄	50979.574	318.21	12.8	³ I ₅ ^o	59085.825	254.39	2.0
		13.0(8) ^b		t ³ H ₆ ^o	60365.631	243.97	2.1
f ⁷ D ₂	50998.641	321.59	7.5	t ³ H ₅ ^o	60549.110	244.26	2.1
				t ³ H ₄ ^o	60757.600	244.01, 249.20	2.1

*The uncertainty of our value in the last column is the larger of $\pm 5\%$ or ± 0.2 ns. Other values measured by laser fluorescence are listed below our result. The uncertainty in the last digit(s) of the other values appears in parentheses.

^aRef. 10, ^bRef. 11, ^cRef. 12, ^dRef. 13, ^eRef. 14, ^fRef. 15.

value) lifetimes for 31 levels that have been measured by other groups¹⁰⁻¹⁵ using laser-induced fluorescence. The uncertainty in the last digit(s) of each entry is enclosed in parentheses following the entry. Our measurements of these level lifetimes agree within the combined error estimates in essentially every case.

3. TRANSITION PROBABILITIES FROM LEVEL LIFETIMES

Given the radiative lifetime τ_u of excited level u , the transition probability A_{ul} for the transition from level u to level l is given by

$$A_{ul} = \text{BF}_{ul}/\tau_u, \quad (1)$$

where BF_{ul} is the emission branching fraction for the transition. We find BF_{ul} from the line intensities $\text{BF}_{ul} = I_{ul}/\sum_{l'} I_{ul'}$, where I is the intensity (in photons per second) of a line after correction for spectrometer response and the sum is taken over all lower levels l' to which the upper level u decays. The spectrophotometry of the line intensities is standard and has been described in detail in Ref. 1; only a summary of the significant parameters will be presented here.

Fourteen spectra, all recorded on the 1-m Fourier-transform spectrometer¹⁶ (FTS) at the National Solar Observatory, Kitt Peak, were measured with the automated DECOMP program that fits a Voigt profile to an observed line to find the line-center wave number and the integrated line area. Nine of the spectra were recorded with a hollow-cathode source¹⁷ operating at a few Torr of pressure of Ar, Ar + Ne, or Ar + He and at source power levels between 17 and 140 W/cm³ of cathode cavity. Si diodes (250–1000 nm), InSb diodes (1000–5000 nm), and solar-blind photoelectric detectors (225–300 nm) were used for different spectral ranges.

The response of the spectrometer system was determined internally for each spectrum from the observed intensity of Ar lines whose true intensity ratios are known, as described in Ref. 1. We extended this branching-ratio method for calibrating spectrometer response into the IR in this experiment by using He line pairs that span the range 400–3300 nm to calibrate a broad range spectrum in which an InSb IR detector was installed on one of the FTS exit channels and a UV Si detector on the other. The use of the two exit channels of the FTS as independent spectrometers was described by Wiese *et al.*¹⁸ The He transition strengths were calculated most recently by Fernley *et al.*,¹⁹ and we used their values for this calibration.

Five spectra measured for this experiment were excited in an inductively coupled Ar plasma source that contained a trace of Fe(CO)₅ and operated at 27 MHz, 1 kW, and 600 Torr of Ar. The distinctive features of the ICP spectrum were discussed in Ref. 1, and we mention only two that we exploit in this work: the broad linewidth (from Doppler broadening at ~7000 K) and the distribution of excited-level populations, which we discuss in Section 5. Emission spectrophotometry is always threatened by self-absorption, a threat that increases as the linewidth narrows. We found that the extremely broad lines of the ICP source are much less prone to self-absorption than are those of the hollow-cathode source, and we measured the

intensity of strong decay channels on the ICP spectra whenever possible.

The population of excited levels in the ICP falls off exponentially as the excitation increases, so that the ICP spectrum is most useful for lines from lower levels, which are, fortunately, those most likely to be self-absorbed. To guard against self-absorption of lines from higher levels that could be measured only on the hollow-cathode spectrum, we used the standard technique of decreasing the source power until line-intensity ratios held constant. We also used an attractive feature of the DECOMP program: After fitting the parameters of a Voigt profile to the observed line, DECOMP displays the residual difference between the observed line and the Voigt profile. Self-absorption produces a characteristic symmetrical double-humped residual that is easily recognized long before any sign of self-absorption is apparent in the experimental line shape.

Although the ICP is an Ar plasma, Ar lines are not prominent in our ICP spectra and cannot be used to calibrate the response. Instead we used well-known Fe branching ratios to establish reference points on the response curve and filled in between these points with the observed response to a commercial W-ribbon radiance standard.

Line-intensity ratios on the 14 measured spectra were intercompared, averaged, and combined so we could find the branching fractions for levels of measured lifetimes. We believe that we have included in the sum in Eq. (1) all significant transitions, because we chose for lifetime measurement only levels that are known or expected to decay within the 4000–45000 cm⁻¹ range of our spectra. Our expectation derives from the semiempirical branching ratios computed by Kurucz⁴; in Section 5 we test his theoretical predictions against experiment and find their accuracy to be adequate for this purpose.

With the radiative lifetimes of Table 1, our experimental branching fractions yield 1174 transition probabilities. A sample of these results are shown in Table 2. The fractional uncertainty $\pm \Delta A/A$ in the transition probability shown in parentheses for each line includes contributions from the uncertainty in the lifetime (5–10%), from the uncertainty ΔI in each line intensity included in the branching fraction, and from the uncertainty in the response function. For ΔI we use the empirical function of the signal-to-noise ratio deduced by Faires *et al.*²⁰ The response function $R(\lambda)$ contributes to the uncertainty ΔBF (and hence to ΔA) in a complex way because it is only the relative response $[R(\lambda_l)/R(\lambda_{l'})]$ that is significant. The uncertainty in this ratio increases as the separation $\lambda_l - \lambda_{l'}$ increases. We have assumed a linear dependence on line separation:

$$\Delta[R(\lambda_l)/R(\lambda_{l'})] = 10^{-5}(\lambda_l - \lambda_{l'})[R(\lambda_l)/R(\lambda_{l'})],$$

with a proportionality constant of 0.001% per wave number, based on our experience with the branching-ratio method for calibrating spectrometer response. With this assumption the response function makes by far the largest contribution to the ΔA for lines that are far removed from the strongest decay channels. We test the reliability of our uncertainty estimates in Section 5.

Table 2. Transition Probability for 478 Strong Lines in Fe I*

Vacuum Waveno.	λ (nm)	Trans. Prob. ($10^7 s^{-1}$)	Upper Level	Lower Level	23872.186	418.7795	1.68	$\pm 6\%$	e^7D_3	$z^7D_4^o$	L		
12161.550	822.0376	1.69	12%	e^5F_5	$z^5G_6^o$	P	23876.499	418.7039	2.33	6%	e^7D_2	$z^7D_3^o$	L
13310.107	751.1019	1.35	$\pm 9\%$	e^5F_5	$y^5F_6^o$	P	23906.669	418.1755	2.32	9%	$^5D_3^o$	b^3P_2	P
17894.508	558.6756	2.19	9%	e^5D_3	$z^5F_5^o$	P	23941.700	417.5636	1.14	9%	$^3D_2^o$	b^3P_1	P
18461.410	541.5199	7.68	5%	e^3H_6	$z^3G_5^o$	L	24044.520	415.7780	2.18	5%	f^5F_3	$z^5F_2^o$	L
18476.044	541.0910	6.33	5%	e^3H_4	$z^3G_3^o$	L	24050.193	415.6799	1.20	9%	$^3D_2^o$	b^3P_2	P
18476.044	541.0910	6.33	5%	e^3H_4	$z^3G_3^o$	L	24061.732	415.4805	1.40	7%	e^7G_5	$z^5F_4^o$	L
18499.146	540.4153	6.92	5%	e^3H_5	$z^3G_4^o$	L	24063.509	415.4499	2.64	10%	$y^3P_1^o$	b^3P_2	P
18570.564	538.3369	7.81	5%	e^5H_6	$z^5G_5^o$	L	24066.980	415.3899	2.05	5%	f^5F_4	$z^5F_3^o$	L
18616.929	536.9962	7.22	5%	e^5H_5	$z^5G_4^o$	L	24125.240	414.3868	1.33	5%	$y^3F_4^o$	a^3F_3	L
18625.583	536.7467	7.13	7%	e^5H_4	$z^5G_3^o$	L	24127.880	414.3414	2.70	9%	$y^1G_4^o$	a^1G_4	P
18634.595	536.4871	5.60	12%	e^5H_3	$z^5G_3^o$	P	24165.303	413.6998	2.75	9%	$y^1D_2^o$	a^1P_1	P
18982.460	526.6555	1.10	7%	e^7D_4	$z^7P_3^o$	L	24178.863	413.4678	1.25	11%	$^3D_3^o$	b^3P_2	P
19104.398	523.2940	1.94	5%	e^7D_5	$z^7P_4^o$	L	24194.191	413.2058	1.18	5%	$y^3F_3^o$	a^3F_2	L
19126.613	522.6862	1.36	7%	e^7D_2	$z^7P_2^o$	L	24220.277	412.7608	1.43	9%	$^3D_1^o$	b^3P_0	P
19253.763	519.2344	1.34	6%	e^7D_3	$z^7P_3^o$	L	24273.572	411.8545	4.96	9%	$z^1I_6^o$	a^1H_5	P
19257.061	519.1455	2.32	7%	e^7D_1	$z^7P_2^o$	L	24325.211	410.9802	1.51	9%	$^3D_1^o$	b^3P_1	P
19934.849	501.4942	2.64	13%	e^3D_2	$z^3F_3^o$	P	24338.911	410.7488	1.74	9%	$^5D_1^o$	b^3P_2	P
20053.567	498.5253	1.48	9%	e^3D_2	$z^3D_2^o$	P	24523.147	407.6629	1.32	10%	f^5D_4	$z^5D_4^o$	P
20165.436	495.7597	4.22	5%	e^7D_5	$z^7F_6^o$	L	24540.401	407.3763	1.68	10%	f^5D_1	$z^5D_2^o$	P
20166.650	495.7298	1.18	7%	e^7D_4	$z^7F_6^o$	L	24552.605	407.1738	7.89	5%	$y^3F_2^o$	a^3F_2	L
20317.455	492.0503	3.58	6%	e^7D_4	$z^7F_5^o$	L	24575.300	406.7978	1.51	9%	e^7P_4	$z^5D_4^o$	P
20323.688	491.8994	1.79	7%	e^7D_3	$z^7F_3^o$	L	24601.810	406.3594	6.66	5%	$y^3F_3^o$	a^3F_3	L
20437.953	489.1492	3.08	5%	e^7D_3	$z^7F_4^o$	L	24608.793	406.2441	1.85	11%	$y^3S_0^o$	b^3P_1	P
20441.033	489.0755	2.25	5%	e^7D_2	$z^7F_2^o$	L	24709.935	404.5812	8.71	5%	$y^3F_4^o$	a^3F_4	L
20493.595	487.8211	1.21	5%	e^7D_1	$z^7F_0^o$	L	24902.472	401.4531	1.53	11%	$z^1X_3^o$	a^1G_4	P
20519.141	487.2138	2.54	5%	e^7D_1	$z^7F_1^o$	L	24960.224	400.5242	2.17	5%	$y^3F_2^o$	a^3F_3	L
20522.593	487.1318	2.44	5%	e^7D_2	$z^7F_3^o$	L	25009.238	399.7392	1.26	5%	$z^3H_5^o$	a^3G_4	L
20571.481	485.9741	1.62	6%	e^7D_1	$z^7F_2^o$	L	25139.911	397.6614	1.20	11%	$^3D_2^o$	a^1P_1	P
22368.213	446.9376	1.59	17%	e^5P_3	$z^5P_2^o$	P	25186.506	396.9257	2.26	5%	$y^3F_3^o$	a^3F_4	L
22382.355	446.6552	1.20	6%	$x^3D_3^o$	b^3P_2	L	25198.165	396.7421	1.52	9%	$u^3G_3^o$	b^3H_4	P
22643.069	441.5123	1.17	6%	$z^5G_3^o$	a^3F_2	L	25264.407	395.7018	1.67	5%	f^5F_3	$z^5D_2^o$	L
22696.388	440.4750	2.72	5%	$z^5G_4^o$	a^3F_3	L	25266.585	395.6677	1.22	5%	$z^3H_6^o$	a^3G_5	L
22806.179	438.3545	5.09	5%	$z^5G_5^o$	a^3F_4	L	25268.000	395.6455	1.76	9%	$u^3G_5^o$	b^3H_6	P
23103.691	432.7096	1.12	9%	$y^1D_2^o$	a^1D_2	P	25301.842	395.1163	4.29	10%	$y^1D_2^o$	a^3D_1	P
23110.816	432.5762	5.16	5%	$z^3G_3^o$	a^3F_2	L	25317.146	394.8775	2.08	9%	$u^3G_4^o$	b^3H_5	P
23206.628	430.7902	3.38	6%	$z^3G_4^o$	a^3F_3	L	25321.499	394.8096	1.31	7%	f^5F_4	$z^5D_3^o$	L
23253.412	429.9235	1.29	5%	e^7D_5	$z^7D_4^o$	L	25400.524	393.5812	1.14	12%	$y^5F_2^o$	b^3P_2	P
23344.807	428.2403	1.21	5%	$z^5S_0^o$	a^5P_3	L	25464.388	392.5941	1.67	12%	$x^3P_0^o$	b^3P_0	P
23402.966	427.1761	2.23	6%	$z^3G_5^o$	a^3F_4	L	25511.822	391.8642	1.17	11%	$v^3G_3^o$	b^3G_3	L
23406.291	427.1154	1.87	6%	e^7D_4	$z^7D_3^o$	L	25513.295	391.8415	4.23	13%	$x^3P_0^o$	b^3P_1	P
23464.961	426.0474	3.99	7%	e^7D_5	$z^7D_5^o$	L	25614.417	390.2946	2.26	5%	$y^3D_3^o$	a^3F_3	L
23522.129	425.0119	2.20	6%	e^7D_3	$z^7D_2^o$	L	25686.934	389.1927	2.71	15%	$^3P_1^o$	a^1P_1	P
23537.048	424.7425	1.94	9%	e^5G_5	$z^5F_4^o$	L	25707.444	388.8822	1.95	15%	$w^3P_1^o$	c^3P_2	P
23584.887	423.8810	2.41	5%	e^5G_4	$z^5F_3^o$	L	25709.483	388.8514	2.50	5%	$y^3D_2^o$	a^3F_2	L
23600.883	423.5937	2.00	6%	e^7D_4	$z^7D_4^o$	L	25744.132	388.3280	1.28	13%	$u^3D_3^o$	a^3D_3	P
23613.894	423.3603	1.96	6%	e^7D_2	$z^7D_0^o$	L	25774.354	387.8726	5.34	11%	$^1P_1^o$	a^3D_1	P
23648.393	422.7427	5.30	7%	e^5G_6	$z^5F_5^o$	L	25815.785	387.2501	1.14	9%	$y^5D_2^o$	a^5F_2	L
23659.431	422.5454	1.65	6%	e^5G_3	$z^5F_2^o$	L	25851.066	386.7216	3.16	10%	$w^3P_2^o$	c^3P_2	P
23688.090	422.0342	1.83	12%	$x^3P_0^o$	c^3P_1	P	25862.387	386.5523	1.67	8%	$y^5D_1^o$	a^5F_1	L
23693.601	421.9360	2.88	5%	$y^3I_6^o$	a^1H_5	L	25966.886	384.9967	6.16	7%	$y^5D_0^o$	a^5F_1	L
23703.797	421.7545	2.46	6%	e^5G_2	$z^5F_1^o$	L	25988.262	384.6800	6.21	9%	$^3D_3^o$	a^3D_3	P
23744.342	421.0344	1.48	9%	e^7D_1	$z^7D_1^o$	L	25990.900	384.6410	1.68	13%	$w^1G_4^o$	a^1H_5	P
23807.946	419.9095	4.92	9%	$z^1H_5^o$	a^1G_4	P	26012.220	384.3257	3.70	9%	$z^1F_3^o$	a^1G_4	P
23810.561	419.8634	1.25	9%	e^5G_2	$z^5F_2^o$	L	26027.178	384.1048	13.6	5%	$y^3D_1^o$	a^3F_2	L
23812.758	419.8247	1.47	5%	e^5G_4	$z^5F_4^o$	L	26031.316	384.0438	4.80	6%	$y^5D_1^o$	a^5F_2	L
23829.318	419.5329	1.11	8%	e^5G_5	$z^5F_5^o$	L	26039.327	383.9256	2.35	10%	$x^1G_4^o$	a^1G_4	P
23851.482	419.1431	2.73	10%	e^7D_1	$z^7D_2^o$	L	26059.184	383.6330	3.29	11%	$^3D_2^o$	a^3D_2	P

Vacuum Waveno.	λ (nm)	Trans. Prob. ($10^7 s^{-1}$)	Upper Level	Lower Level	27405.653	364.7843	3.29	$\pm 6\%$	$z^5G_5^o$	a^5F_4	L		
					27408.805	364.7423	3.38	10%	$1^1P_1^o$	c^3P_1	P		
26073.510	383.4223	4.88	$\pm 9\%$	$y^5D_2^o$	a^5F_3	L	27420.857	364.5820	4.87	11%	$u^3D_1^o$	c^3P_0	P
26105.995	382.9451	1.32	18%	$u^3D_1^o$	a^3D_1	P	27461.768	364.0389	3.58	5%	$v^3G_5^o$	a^3G_4	L
26117.101	382.7823	11.3	5%	$y^3D_2^o$	a^3F_3	L	27477.558	363.8297	2.36	5%	$y^3H_4^o$	a^3G_3	L
26130.356	382.5881	6.15	5%	$y^5D_3^o$	a^5F_4	L	27493.222	363.6224	2.20	10%	$1^1F_3^o$	a^1D_2	P
26162.516	382.1178	5.54	5%	$y^3I_6^o$	b^3H_5	L	27524.899	363.2039	6.75	9%	$u^3D_2^o$	c^3P_1	P
26167.670	382.0425	7.29	7%	$y^5D_2^o$	a^5P_5	L	27529.262	363.1463	5.62	5%	$z^5G_4^o$	a^5F_3	L
26199.112	381.5840	11.3	5%	$y^3D_3^o$	a^3F_4	L	27532.037	363.1097	2.15	9%	$f^7D_5^o$	$z^7F_5^o$	L
26234.069	381.0756	1.94	11%	$3^1D_1^o$	a^3D_2	P	27601.159	362.2004	5.14	5%	$v^3G_3^o$	a^3G_3	L
26262.047	380.6696	4.35	6%	$w^3H_5^o$	b^3H_5	L	27605.296	362.1461	4.46	5%	$y^3H_5^o$	a^3G_4	L
26271.384	380.5343	8.60	5%	$y^3I_5^o$	b^3H_4	L	27625.837	361.8768	7.22	5%	$z^5G_3^o$	a^5F_2	L
26325.535	379.7515	4.57	6%	$w^3H_6^o$	b^3H_6	L	27633.334	361.7786	7.10	9%	$u^3D_3^o$	c^3P_2	P
26342.965	379.5002	1.20	7%	$y^5F_3^o$	a^5F_2	L	27677.073	361.2069	1.11	7%	e^5G_6	$z^7F_5^o$	L
26392.495	378.7880	1.35	5%	$y^5F_2^o$	a^5F_1	L	27691.712	361.0159	5.90	11%	e^7F_6	$z^7F_6^o$	L
26457.949	377.8509	1.17	13%	$3^1D_2^o$	a^3D_3	P	27701.686	360.8859	8.32	5%	$z^5G_2^o$	a^5F_1	L
26537.432	376.7192	6.50	5%	$y^5F_1^o$	a^5F_1	L	27718.427	360.6680	8.30	5%	$y^3H_6^o$	a^3G_5	L
26549.079	376.5539	9.51	5%	$y^3I_7^o$	b^3H_6	L	27727.490	360.5501	2.12	9%	f^7D_5	$z^7F_6^o$	L
26561.423	376.3789	5.66	5%	$y^5F_2^o$	a^5F_2	L	27727.857	360.5453	4.67	5%	$y^3H_4^o$	a^3G_4	L
26600.690	375.8233	6.66	5%	$y^5F_3^o$	a^5F_3	L	27740.436	360.3818	1.70	11%	$u^3D_1^o$	c^3P_1	P
26633.443	375.3611	1.22	21%	$w^5D_2^o$	a^5P_3	L	27745.165	360.3204	2.59	5%	$v^3G_5^o$	a^3G_5	L
26662.749	374.9485	8.16	6%	$y^5F_4^o$	a^5F_4	L	27750.386	360.2526	2.12	12%	e^7P_2	$z^7F_3^o$	P
26666.449	374.8965	1.48	9%	f^7D_5	$z^7P_4^o$	L	27772.743	359.9626	2.33	6%	$u^3F_4^o$	a^1H_5	L
26680.952	374.6927	2.33	6%	f^7D_3	$z^7P_3^o$	L	27811.321	359.4632	3.14	6%	f^7D_4	$z^7F_4^o$	L
26690.681	374.5561	1.16	5%	$z^5F_3^o$	a^5D_2	L	27855.610	358.8917	2.15	11%	f^7D_1	$z^7F_2^o$	L
26701.077	374.4103	3.17	7%	e^7F_1	$z^7P_2^o$	L	27858.000	358.8609	1.19	7%	e^5G_5	$z^7F_5^o$	L
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(continued overleaf)

Table 2. Continued

Vacuum Waveno.	λ (nm)	Trans. Prob. (10^7s^{-1})	Upper Level	Lower Level	31124.388	321.1987	4.64 $\pm 9\%$	$e^7 P_4$	$z^7 D_0^o$	P	
28844.601	346.5861	1.19 $\pm 8\%$	$z^5 P_0^1$	$a^5 D_1$	P	31135.605	321.0830	9.25 5%	$f^7 D_1$	$z^7 D_2^o$	L
28894.170	345.9915	2.17 9%	$^3 P_1^1$	$c^3 P_2$	P	31141.426	321.0229	1.15 6%	$e^5 G_5$	$z^7 D_4^o$	L
28907.629	345.8304	2.92 10%	$x^3 P_0^1$	$a^3 P_1$	P	31188.360	320.5398	9.78 5%	$e^7 F_1$	$z^7 D_1^o$	L
28961.133	345.1915	1.13 9%	$^3 D_2^o$	$a^5 P_1$	P	31245.556	319.9530	2.23 5%	$f^7 D_4$	$z^7 D_1^o$	L
28974.449	345.0328	2.34 9%	$y^3 P_1^1$	$a^5 P_1$	P	31270.994	319.6928	5.97 5%	$e^7 F_5$	$z^7 D_4^o$	L
29018.003	344.5149	2.34 9%	$^5 D_3^o$	$a^5 P_2$	P	31278.867	319.6123	1.40 5%	$g^7 D_4$	$z^7 F_5^o$	L
29053.088	344.0989	1.24 8%	$z^5 P_2^1$	$a^5 D_3$	P	31306.517	319.3300	3.07 5%	$e^5 G_3$	$z^7 D_2^o$	L
29056.320	344.0606	1.71 8%	$z^5 P_3^1$	$a^5 D_4$	P	31311.414	319.2801	5.01 5%	$e^7 F_2$	$z^7 D_0^o$	L
29161.527	342.8193	1.71 10%	$^3 D_2^o$	$a^5 P_2$	P	31350.507	318.8819	2.53 6%	$e^5 G_2$	$z^7 D_1^o$	L
29170.658	342.7120	5.04 9%	$^5 D_4^o$	$a^5 P_3$	P	31408.070	318.2975	1.42 15%	$g^7 D_3$	$z^7 F_4^o$	L
29174.845	342.6628	1.94 9%	$y^3 P_0^1$	$a^5 P_2$	P	31422.437	318.1519	1.84 10%	$u^3 D_2^o$	$b^3 F_3$	P
29188.623	342.5010	2.57 11%	$x^3 F_3^o$	$a^1 G_4$	P	31435.238	318.0224	4.42 6%	$e^7 F_4$	$z^7 D_3^o$	L
29194.809	342.4285	1.61 9%	$^5 D_3^o$	$a^5 P_3$	P	31457.101	317.8013	1.28 6%	$f^7 D_4$	$z^7 D_5^o$	L
29208.699	342.2656	1.38 9%	$^5 D_2^o$	$a^5 P_1$	P	31482.542	317.5445	1.44 6%	$e^7 F_5$	$z^7 D_5^o$	L
29244.147	341.8507	9.89 9%	$^5 D_0^o$	$a^5 P_1$	P	31523.181	317.1351	1.85 10%	$^1 F_3^o$	$a^1 G_4$	P
29249.850	341.7841	4.01 9%	$^5 D_1^o$	$a^5 P_1$	P	31572.115	316.6436	1.56 14%	$^3 D_3^o$	$b^3 F_4$	P
29290.197	341.3133	3.23 9%	$^3 D_3^o$	$a^5 P_2$	P	31629.832	316.0657	1.93 6%	$e^7 F_4$	$z^7 D_4^o$	L
29315.648	341.0169	5.07 12%	$u^3 F_2^o$	$a^1 P_1$	P	31657.602	315.7885	1.61 11%	$e^7 S_3$	$z^7 D_2^o$	L
29338.957	340.7460	6.09 9%	$^3 F_4^o$	$a^5 P_3$	P	31666.111	315.7036	1.26 6%	$e^7 G_5$	$z^7 D_2^o$	L
29344.642	340.6800	2.08 10%	$^3 D_1^o$	$a^5 P_1$	P	31673.756	315.6274	6.36 11%	$i^5 D_3$	$z^5 D_3^o$	P
29383.828	340.2256	2.19 11%	$^3 H_6^o$	$b^3 H_6$	L	31797.487	314.3992	6.10 10%	$i^5 D_4$	$z^5 D_4^o$	P
29409.093	339.9333	2.76 9%	$^5 D_2^o$	$a^5 P_2$	P	31913.941	313.2519	3.39 14%	$i^5 D_3$	$z^5 D_4^o$	P
29467.004	339.2653	1.88 9%	$^3 D_3^o$	$a^5 P_3$	P	32241.790	310.0665	1.35 21%	$x^5 D_3^o$	$a^5 F_3$	L
29576.342	338.0110	1.66 10%	$u^3 G_3^o$	$a^3 G_3$	P	32245.548	310.0304	1.87 13%	$x^5 D_2^o$	$a^5 F_2$	L
29658.174	337.0784	2.89 9%	$u^3 G_5^o$	$a^3 G_5$	P	32249.802	309.9895	1.93 13%	$x^5 D_1^o$	$a^5 F_1$	L
29669.053	336.9548	2.15 10%	$u^3 G_4^o$	$a^3 G_4$	P	32336.568	309.1577	5.53 21%	$x^5 D_0^o$	$a^5 F_1$ </	

Table 2. Continued

Vacuum Waveno.	λ (nm)	Trans. Prob. ($10^7 s^{-1}$)	Upper Level	Lower Level									
33714.070	296.5255	1.28 $\pm 7\%$	$y^5F_1^o$	a^5D_0	L	37315.413	267.9062	1.50 $\pm 5\%$	$^5F_5^o$	a^5F_5	L		
33774.003	295.9993	5.02 7%	$^3H_6^o$	a^3G_5	L	37315.957	267.9023	1.10 9%	$x^3F_5^o$	a^3H_4	L		
33802.644	295.7484	1.31 18%	$^1P_1^o$	a^3P_2	P	37449.157	266.9493	1.34 7%	$x^3F_6^o$	a^3H_5	L		
33804.012	295.7365	1.84 7%	$y^5F_1^o$	a^5D_1	L	37637.340	265.6145	1.63 7%	$x^3F_7^o$	a^3H_6	L		
33843.199	295.3940	1.96 8%	$y^5F_2^o$	a^5D_2	L	37810.240	264.3999	2.34 5%	$x^5G_2^o$	a^5F_1	L		
33848.404	295.3486	3.64 11%	$^1F_3^o$	a^3G_3	P	37927.713	263.5809	2.11 5%	$x^5G_3^o$	a^5F_2	L		
33906.400	294.8434	3.32 10%	$^3G_4^o$	a^3G_4	P	37979.169	263.2238	1.21 5%	$x^5G_2^o$	a^5F_2	L		
33912.815	294.7876	1.83 7%	$y^5F_3^o$	a^5D_3	L	38105.159	262.3534	2.13 5%	$x^5G_3^o$	a^5F_3	L		
34039.510	293.6904	1.40 11%	$y^5F_4^o$	a^5D_4	L	38185.438	261.8018	1.50 5%	$x^5G_3^o$	a^5F_3	L		
34130.004	292.9116	15.3 14%	$t^3H_4^o$	b^3H_4	L	38314.173	260.9221	4.60 13%	$^3G_3^o$	a^3G_3	P		
34173.851	292.5358	1.69 9%	u^3H_4	a^3G_3	L	38349.364	260.6827	2.43 5%	$x^5G_5^o$	a^5F_4	L		
34191.442	292.3853	2.97 10%	$^1H_5^o$	a^3G_5	P	38456.456	259.9567	1.47 5%	$x^5G_2^o$	a^5F_4	L		
34198.075	292.3286	13.9 14%	$t^3H_5^o$	b^3H_5	L	38680.091	258.4536	3.15 5%	$x^5G_6^o$	a^5F_5	L		
34259.726	291.8025	11.8 14%	$t^3H_6^o$	b^3H_6	L	38797.860	257.6690	1.13 5%	$x^5G_5^o$	a^5F_5	L		
34383.530	290.7518	1.61 9%	u^3H_5	a^3G_4	L	39209.861	254.9614	2.31 10%	$x^5D_4^o$	a^5D_3	P		
34449.963	290.1910	1.78 6%	g^7D_5	$z^7D_5^o$	L	39265.842	254.5978	7.16 13%	$x^5D_3^o$	a^5D_2	L		
34479.617	289.9415	4.68 11%	$^3D_1^o$	a^3P_2	P	39297.577	254.3922	47.1 10%	$^3F_5^o$	a^3H_4	L		
34538.105	289.4504	4.83 10%	$^3P_2^o$	a^3P_2	P	39325.725	254.2101	44.8 13%	$^3F_6^o$	a^3H_5	L		
34851.757	286.8454	1.45 10%	$^3P_1^o$	a^3P_2	P	39343.201	254.0972	9.60 13%	$x^5D_2^o$	a^5D_1	L		
35055.310	285.1797	3.37 5%	$y^5G_2^o$	a^5F_1	L	39402.083	253.7175	37.0 7%	$^3F_7^o$	a^3H_6	L		
35151.701	284.3977	3.17 5%	$y^5G_3^o$	a^5F_2	L	39426.439	253.5607	9.58 9%	$x^5D_1^o$	a^5D_0	L		
35224.237	283.8120	1.28 5%	$y^5G_2^o$	a^5F_2	L	39464.814	253.3141	2.07 12%	$^3F_5^o$	a^3H_5	L		
35294.921	283.2436	2.38 5%	$y^5G_4^o$	a^5F_3	L	39516.383	252.9835	3.84 9%	$x^5D_1^o$	a^5D_1	L		
35380.854	282.5556	1.32 5%	$z^5H_4^o$	a^5F_3	L	39524.621	252.9308	48.7 10%	$^3G_3^o$	b^3F_2	P		
35409.425	282.3276	1.51 5%	$y^5G_3^o$	a^5F_3	L	39527.326	252.9135	9.92 10%	$x^5D_3^o$	a^5D_2	L		
35535.150	281.3287	3.42 5%	$y^5G_5^o$	a^5F_4	L	39553.916	252.7435	19.3 9%	$x^5D_3^o$	a^5D_3	L		
35614.929	280.6984	1.15 5%	$z^5H_5^o$	a^5F_4	L	39556.545	252.7267	3.47 27%	$^3F_6^o$	a^3H_6	L		
35641.874	280.4862	2.40 26%	$t^3F_3^o$	a^3G_4	L	39603.150	252.4292	32.3 8%	$x^5D_6^o$	a^5D_1	L		
35834.279	278.9801	2.36 6%	$t^3F_4^o$	a^3G_5	L	39625.790	252.2850	21.3 9%	$x^5D_4^o$	a^5D_4	P		
35856.082	278.8105	5.92 5%	$y^5G_6^o$	a^5F_5	L	39676.437	251.9629	1.34 11%	$w^5G_2^o$	a^5F_1	L		
36099.571	276.9298	1.80 11%	$^3H_6^o$	a^3H_6	L	39700.506	251.8102	19.3 8%	$x^5D_1^o$	a^5D_2	L		
36122.747	276.7521	1.48 16%	$w^5D_4^o$	a^5F_4	L	39707.452	251.7661	1.58 7%	$w^5G_3^o$	a^5F_2	L		
36194.606	276.2027	1.76 26%	$w^5D_3^o$	a^5F_3	L	39815.400	251.0835	12.9 8%	$x^5D_5^o$	a^5D_3	L		
36197.839	276.1780	1.94 5%	$w^5D_2^o$	a^5F_2	L	39861.986	250.7900	1.93 5%	$w^5G_4^o$	a^5F_3	L		
36256.443	275.7316	2.85 5%	$w^5D_1^o$	a^5F_1	L	39883.123	250.6571	2.04 14%	$t^3H_4^o$	b^3F_3	L		
36269.431	275.6328	1.41 7%	$y^5P_2^o$	a^5D_1	L	39908.011	250.5008	2.56 16%	$t^3H_5^o$	b^3F_4	L		
36304.217	275.3687	4.00 7%	$w^5D_0^o$	a^5F_1	L	39969.849	250.1132	6.76 13%	$x^5D_3^o$	a^5D_4	L		
36351.027	275.0141	2.74 7%	$y^5P_3^o$	a^5D_3	L	40043.462	249.6534	2.15 9%	$w^5G_5^o$	a^5F_4	L		
36425.371	274.4528	2.53 5%	$w^5D_1^o$	a^5F_2	L	40116.485	249.1989	3.25 27%	$t^3H_4^o$	b^3F_4	L		
36431.476	274.4068	3.09 7%	$y^5P_1^o$	a^5D_0	L	40129.915	249.1155	29.1 10%	$x^5F_2^o$	a^5D_2	L		
36453.554	274.2406	4.70 11%	$y^5P_2^o$	a^5D_2	L	40138.143	249.0644	34.5 10%	$x^5F_3^o$	a^5D_2	L		
36455.564	274.2254	3.41 11%	$w^5D_2^o$	a^5F_3	L	40152.521	248.9752	23.1 11%	$x^5F_1^o$	a^5D_0	L		
36517.002	273.7640	1.14 10%	$^1H_5^o$	a^3H_6	P	40178.491	248.8143	42.0 10%	$x^5F_4^o$	a^5D_3	L		
36521.417	273.7309	7.25 7%	$y^5P_1^o$	a^5D_1	L	40195.890	248.7066	6.41 12%	$v^5F_4^o$	a^5F_1	P		
36545.901	273.5475	5.03 26%	$w^5D_3^o$	a^5F_4	L	40201.935	248.6692	1.47 10%	$v^5F_3^o$	a^5F_3	P		
36571.233	273.3581	7.10 11%	$w^5D_4^o$	a^5F_5	L	40242.462	248.4188	22.6 11%	$x^5F_1^o$	a^5D_1	L		
36635.028	272.8820	2.98 7%	$u^3H_4^o$	a^3H_4	L	40253.059	248.3534	2.09 22%	$v^5F_2^o$	a^5F_2	P		
36672.177	272.6056	5.52 5%	$^5D_0^o$	a^5F_1	L	40257.306	248.3271	48.1 10%	$x^5F_5^o$	a^5D_4	L		
36705.544	272.3577	5.69 9%	$y^5P_1^o$	a^5D_2	L	40314.036	247.9777	17.4 10%	$x^5F_3^o$	a^5D_3	L		
36741.628	272.0902	10.4 7%	$y^5P_2^o$	a^5D_3	L	40318.854	247.9480	2.10 9%	$x^3P_2^o$	a^5F_2	P		
36761.651	271.9420	3.20 6%	$u^3H_5^o$	a^3H_5	L	40364.817	247.6657	3.05 9%	$v^5F_1^o$	a^5F_2	P		
36766.527	271.9060	7.40 7%	$t^3F_3^o$	b^3F_3	L	40394.866	247.4814	6.14 10%	$v^5F_3^o$	a^5F_3	P		
36766.960	271.9028	14.2 5%	$y^5P_3^o$	a^5D_4	L	40426.216	247.2895	13.0 10%	$x^5F_1^o$	a^5D_3	L		
36774.958	271.8436	3.79 5%	$^5D_1^o$	a^5F_2	L	40426.588	247.2872	2.10 22%	$x^5F_1^o$	a^5D_2	L		
36908.896	270.8571	6.49 5%	$t^3F_4^o$	b^3F_4	L	40491.958	246.8880	2.40 6%	$w^5G_5^o$	a^5F_5	L		
36936.015	270.6582	2.69 5%	$^5D_2^o$	a^5F_3	L	40553.230	246.5149	4.36 10%	$v^5F_4^o$	a^5F_4	P		
36943.788	270.6013	2.28 6%	$u^3H_6^o$	a^3H_6	L	40576.583	246.3730	1.64 10%	$x^3P_2^o$	a^5F_3	P		
37174.572	268.9212	1.68 5%	$^5F_3^o$	a^5F_4	L	40594.423	246.2648	5.85 14%	$x^5F_4^o$	a^5D_4	L		
						40602.113	246.2181	1.10 14%	$x^5F_2^o$	a^5D_3	L		
						40677.845	245.7597	4.82 10%	$v^5F_5^o$	a^5F_5	P		

*The last column indicates the method of measurement (lifetime L or level population P). Wavelength (column 2) is in air.

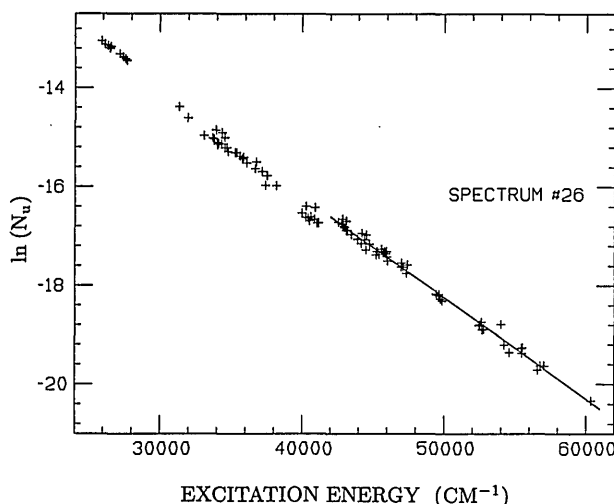


Fig. 2. Logarithm (base e) of the mean relative population per state \bar{N}_u in an ICP spectrum containing a trace of $\text{Fe}(\text{CO})_5$ as a function of level energy. The line segment is a least-squares fit to the population per state of levels above $45\,000\text{ cm}^{-1}$.

4. TRANSITION PROBABILITIES FROM LEVEL POPULATIONS

The measured intensity $I(\lambda)$ (in photons per second) of any line of known transition probability $A(\lambda)$ is related to the population N_u per state of upper level u by

$$I(\lambda) = N_u g A(\lambda), \quad (2)$$

where g is the statistical weight of level u . In this section we use this relation in two ways. First, we find the relative population of excited levels in the ICP source by using the transition probabilities measured in Section 3. Then we interpolate between levels of known population to find the population $N_{u'}$ per state of new levels of unknown lifetime. Second, we use Eq. (2) to convert the intensity of lines from level u' into transition probabilities.

In an earlier study of Mo we found that the relative population per state of excited Mo I levels in the ICP source approximated an exponential dependence on excitation energy, as if the source were in thermal equilibrium. The Fe I populations per state of excited levels do not display such regular and easily understood behavior. It may be that Fe and Mo behave differently in the ICP source; a more likely explanation is that the extensive level information for Fe reveals irregular behavior that could not be seen with the sparse Mo population data.

When several emission lines from a level have been measured, we find a mean value of $\bar{N}_u = \sum_i I_{ui} / g \sum_i A_{ui}$, summed over all the emission transitions from level u seen in an ICP spectrum. This mean value \bar{N}_u is shown in Fig. 2 for a broad-range spectrum (number 26-7/24/85) of an ICP source operated at relatively high power to bring up lines from high levels. The vertical scale is arbitrary: only relative populations are measured.

The population distribution in Fig. 2 shows a small upward concavity, as do all the Fe I ICP spectra that we have examined. A closer examination of individual levels shows further systematic displacements from linearity that can be seen more readily in Fig. 3, where we plot the deviation of experimental values of $\ln(N_u)$ from the straight line segment that best fits a limited region of ex-

citation energy. The horizontal line segment shown at the top of Fig. 3 for spectrum 26 is the same line shown in Fig. 2. Levels with the shortest lifetimes (e.g., the x^5D and x^5F levels near $42\,000\text{ cm}^{-1}$) tend to lie lower than longer-lived levels at nearly the same excitation energy. Likewise, levels of unusually long lifetime tend to have higher populations. This dependence of population on lifetime is similar to but much smaller than that observed in the hollow-cathode source. Fortunately the deviations from a simple exponential distribution are small, and we are able to interpolate between the measured populations to estimate the populations of levels that have not been measured.

Spectrum 26 was taken with high source power, and many of the stronger lines from the lower energy levels are self-absorbed. It is advantageous to use spectra recorded at different source power levels to measure the relative population of levels in different excitation energy ranges. We use spectrum 26 only for levels with energies above $42\,000\text{ cm}^{-1}$, for which self-absorption is not seen on this spectrum. The populations per state fit a straight line with a rms deviation of 9% (see Fig. 3). For spectrum 30-7/25/85, used for levels between $24\,000$ and $42\,000\text{ cm}^{-1}$, the experimental populations per state fit a straight line within 8%. For spectrum 12-7/31/85 the rms deviation is 8%. Filters limited spectrum 12 to the wave-number range $18\,000$ – $25\,000\text{ cm}^{-1}$ in order to reduce the background noise so that the weak lines from the three lowest septet terms could be measured. Lifetimes of the septet levels are too long ($\sim 10^{-4}\text{ s}$) to be measured by the methods of Section 2. The gf values of Blackwell *et al.*² were used to evaluate the population of the four septet levels represented by open circles in Fig. 3.

From the linear least-squares fit to the experimental points shown in Fig. 3 one can estimate the relative population $N_{u'}$ per state of a new level u' of unknown lifetime. For at least one line λ (selected for low noise background and a good fit to the Voigt line profile) emitted from level u' , we measured $I(\lambda)$ on the ICP spectrum and calculated the transition probability $A(\lambda) = I(\lambda)/gN_{u'}$, with fractional

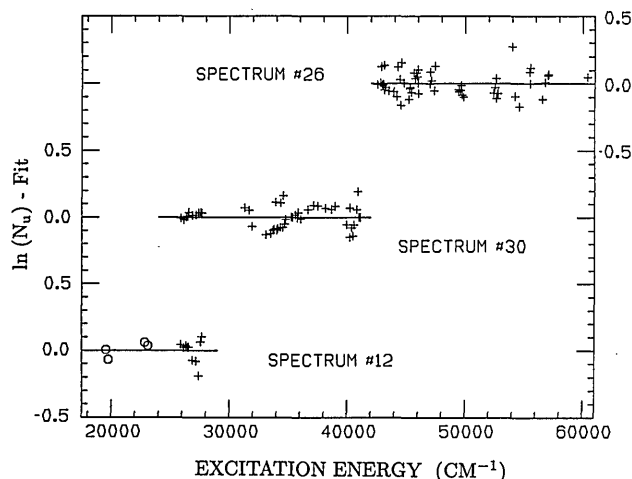


Fig. 3. Difference between $\ln(\bar{N})$ and the least-squares linear fit as a function of level energy, shown here as a horizontal line. The line segment shown for spectrum 26 is the same line as that drawn in Fig. 2; it represents a temperature of 7023 K . Populations per state of the levels represented by open circles were evaluated with gf values of Blackwell *et al.*²

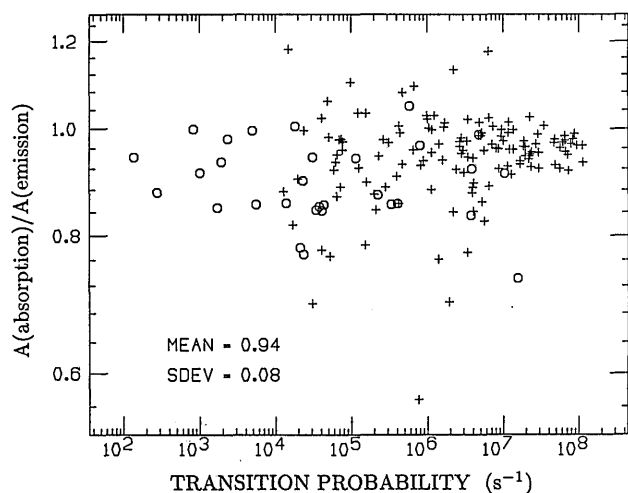


Fig. 4. Ratio of the Oxford transition probability measured in absorption to our value measured in emission for 163 lines. Pluses represent measurements by the lifetime method; circles represent measurements by interpolated level population.

uncertainty $\Delta A/A = [(\Delta I/I)^2 + (\Delta N_u/N_u)^2]^{1/2}$. N_u is read from the linear fit shown in Fig. 3, and for $\Delta N_u/N_u$ we use the rms deviation from the linear fit to the experimental points (i.e., 9% for spectrum 26).

Additional transition probabilities $A(\lambda')$ were found from line-intensity ratios $I(\lambda')/I(\lambda)$ of other lines λ' from level u' : $A(\lambda') = A(\lambda)[I(\lambda')/I(\lambda)]$ with fractional uncertainty $\Delta A'/A' = [(\Delta A/A)^2 + (\Delta I'/I')^2 + (\Delta I/I)^2]^{1/2}$. Note that complete branching fractions, required when A values are found from the level lifetime, are not needed; branching ratios $I(\lambda')/I(\lambda)$ are sufficient, and they can be measured on any spectrum. Some of the 640 transition probabilities from 104 levels measured by the population method, identified with the postscript P, appear in Table 2.

5. RESULTS AND COMPARISON WITH OTHER VALUES

Publication in this journal of all 1814 transition probabilities produced in this experiment is not feasible. In Table 2 we list values for the 478 strongest transitions that we measured. Those who need our complete results will almost certainly prefer to have them in machine-readable form. The complete list in the format of Table 2 may be obtained by BITNET request to WNW@CALTECH or by sending a 5.25 in. diskette (double sided, double density) in a reusable shipping container to W. Whaling. Include a mailing label and specify the density (360K, 1.2M) that should be used in writing the diskette, readable on an IBM or compatible microcomputer. Eventually our complete results will be deposited with the NIST Atomic Transition Probability Data Center.

We compare our transition probabilities first with the absorption oscillator strengths measured by Blackwell and his Oxford co-workers,² widely recognized to be the most precise values available, to justify our assumption concerning the level populations in the ICP source and to confirm the reliability of our uncertainty estimates. In Fig. 4 we plot the ratio of the Oxford transition probability (measured in absorption) to our emission value for 163 lines that are common to both experiments. For 133 lines measured by the lifetime method (represented by pluses in

the figure), the mean value of the ratio $A_{\text{abs}}/A_{\text{emis}}$ is 0.95 with a standard deviation for the sample of 0.08. For 30 lines measured by interpolation of level populations in the ICP source (the circles of Fig. 4), the corresponding ratio is 0.90 ± 0.08 . We find no significant difference between the results of the two different methods. The 8% spread in the ratio $A_{\text{abs}}/A_{\text{emis}}$ is consistent with the fractional uncertainties (in parentheses) assigned to the transition probabilities in Table 2. That this spread is no larger for the values obtained by the population method confirms our confidence in the ICP source as a useful tool for measuring transition probabilities, and the magnitude of the spread validates our uncertainty assignments.

To test the suggestion²¹ of a temperature error in the Oxford measurements, we plot in Fig. 5 the ratio $A_{\text{abs}}/A_{\text{emis}}$ as a function of the energy of the lower level in the transition. We use only stronger lines with minimum uncertainty for this test; the 66 points in Fig. 5 are all the transitions measured at Oxford and by us to which we assign an uncertainty $\leq 6\%$. As first noted by Kock *et al.*,²¹ the ratio appears to be lower (by $\sim 5\%$) for transitions involving levels near $20\,000\text{ cm}^{-1}$ than it is for transitions from lower levels. However, we do not observe the exponential variation with excitation energy that is characteristic of a temperature error in the absorption furnace. Within our experimental uncertainty (5–6% for the points plotted in Fig. 5) the ratio is independent of excitation energy for levels below $14\,000\text{ cm}^{-1}$.

The recent critical compilation by the NIST Atomic Transition Probability Data Center³ contains 728 of the transitions that we have measured. These include the 163 Oxford *gf* values, to which we have already made comparison and therefore exclude from the following discussion, plus an additional 565 values taken from many sources; many of the latter values have been adjusted or renormalized by NIST compilers to conform to the most modern and accurate standards. On average our values agree quite well with these 565 NIST values: The mean value of $\ln(A_{\text{NIST}}/A_{\text{emis}}) = 0.02 \pm 0.35$. The $\pm 42\%$ scatter is reasonable, since the NIST compilation includes values with an uncertainty within $\pm 50\%$.

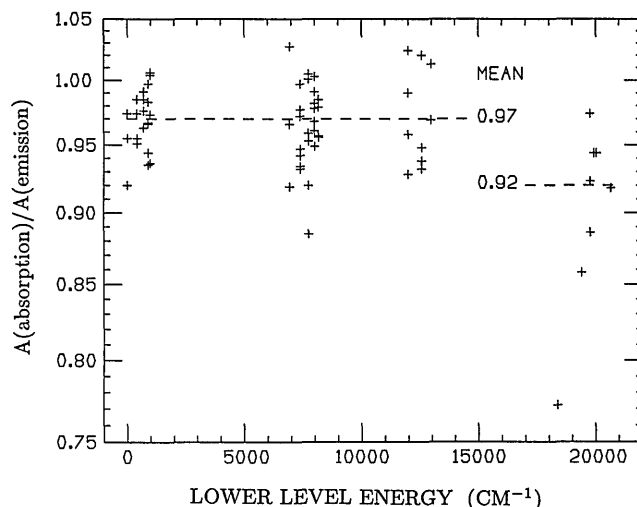


Fig. 5. Ratios from Fig. 4 plotted as a function of lower level energy. Only the strongest 66 lines with uncertainty in $A_{\text{emis}} \leq 6\%$ are shown. The low point at $18\,378\text{ cm}^{-1}$ was ignored for computation of the mean value shown.

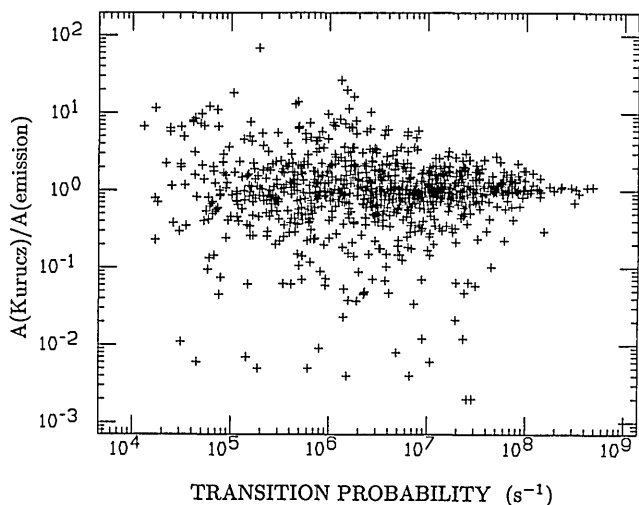


Fig. 6. Ratio of semiempirical transition probabilities computed by Kurucz⁴ to our experimental values. Mean of 1117 values is 0.93. Two thirds of the theoretical values lie within a factor of 3 of the experimental values.

The recent publication by Kock *et al.*²¹ of 122 Fe I transition probabilities appeared too late to be included in the NIST compilation. We have measured 110 of the transitions measured by Kock *et al.* The mean value of $\ln(A_{\text{Kock}}/A_{\text{emis}})$ is 0.02 ± 0.25 .

We made extensive use of the Kurucz semiempirical transition probabilities⁴ in our branching-fraction measurements, and it is of interest to find out how reliable his computed values are by comparing them with experimental values. Figure 6 shows the ratio $A_{\text{Kurucz}}/A_{\text{emis}}$ for 1117 values measured by the lifetime method; a plot of values measured from populations looks much the same. The mean value of the natural logarithm of the ratio is -0.07 ± 1.07 ; two thirds of the theoretical values lie within a factor of 3 of the experimental value. Since Kurucz has calculated essentially every transition between all known energy levels in Fe I, his tables are quite useful when precision of this order is adequate. We used his values in deciding when transitions outside the range of our spectra contribute negligibly to the total transition strength and also when transitions with spin change $\Delta S > 1$ may make a significant contribution.

6. Fe I LEVEL ENERGIES

Identification of lines in our FTS spectrum is based on near coincidence (within $\pm 0.01 \text{ cm}^{-1}$) between the observed vacuum wave number and a predicted transition energy. The predicted line list used for this identification contains all transitions between known Fe I levels that satisfy the conditions parity change, $\delta J = 0, \pm 1$, and $\delta S = 0, \pm 1$.

Line identification on the basis of wavelength alone sets severe requirements for the level energies used in preparing the predicted line list. In addition to the obvious need for precise energies and correct J values (and if possible correct L and S values as well), there is another requirement that we have come to appreciate as we compare spectra from different sources: The level energies must be those appropriate to the spectral source used to produce the spectrum. This requirement can be satisfied

only by determining the level energies from the spectrum itself, i.e., from the observed transition energies. To find level energies that meet these requirements, we carried out the following iterative process.

Step 1. Starting with the energy levels in the 1985 AEL,⁵ we prepared the predicted line list, as described above, containing 12,224 lines between 8000 and 45 000 cm^{-1} .

Step 2. For a selected hollow-cathode spectrum (number 6-2/12/83), covering the range 8000–45 000 cm^{-1} , we measured all lines with a signal-to-noise ratio greater than 3, using the Kitt Peak DECOMP program to fit a Voigt profile to the observed line in order to find the line-center wave number. The observed line list contains 6280 lines, including Fe II, Ar, and Ne as well as Fe I.

Step 3. A computer search for predicted lines within 0.01 cm^{-1} of an observed line produced an identified line list of 2144 Fe I lines. In spite of the small search window, our search program assigned two different classifications to ~ 100 lines; i.e., two predicted lines fell within $\pm 0.01 \text{ cm}^{-1}$ of the observed line. The choice between the two alternative assignments could usually be made on the basis of the semiempirical gf values computed by Kurucz⁴ for the two transitions. If no choice was possible, both lines were deleted. The level energies are greatly overdetermined (2144 transitions to determine 442 levels), so that a few uncertain lines could be dropped with little loss.

Step 4. The observed vacuum wave numbers in the identified line list give precise energy differences $\Delta E_{ij} = E_i - E_j$ between the level energies appropriate to our source, and the ΔE_{ij} 's can be used to find the set of most probable level energies $\{E_i\}$ by the least-squares method. We used the CLEVEL least-squares code of Palmer and Engleman²² to solve for the energies. Their solution assigns to each observed transition $\Delta E_{ij} \pm \delta \Delta E_{ij}$ a weight proportional to $(\delta \Delta E_{ij})^{-2}$, so that a reliable estimate of the experimental uncertainty $\delta \Delta E_{ij}$ becomes an important part of the solution.

Following the analysis of Brault,²³ we take $\delta \Delta E_{ij} = (1/2)\text{FWHM}/(S/N_i)$, where FWHM is the full width at half-maximum of the line of peak amplitude S and N_i is the total noise amplitude. The total noise amplitude N_i has two components: In addition to the usual rms background noise N_c that one sees between lines and measures by moving several linewidths away from the line center a FTS spectrum contains another noise component N_s that is produced by variation in source brightness during the observation. N_s is proportional to the peak amplitude: $N_s = \kappa S$. Unlike N_c , which is nearly independent of wave number, N_s is present only under the line itself and can be seen and measured only after the contribution of the line from the observed spectrum is subtracted. The total noise amplitude is given by $N_i = (N_c^2 + N_s^2)^{1/2}$. The constant κ is sufficiently small (0.006 for spectrum 6-3/12/83) that the N_s is negligible except for the strongest line, where it limits S/N_i to a maximum value of ~ 170 .

We tested our uncertainty estimate by comparing our wave numbers with those of Learner and Thorne,²⁴ who carefully measured 312 stronger Fe I lines as transfer wave-number standards. The average difference between our wave numbers and theirs is consistent with the uncertainty that we estimate by the method described above.

In addition to the statistical uncertainty that depends on linewidth and signal-to-noise ratio there is an uncertainty associated with the alignment factor. If the light beam entering the FTS from the source is not exactly parallel to the He-Ne laser beam that is used to monitor the mirror displacement, one must multiply the wave-number scale of the FTS by a constant factor to correct for the misalignment. We found the alignment factor $F \pm \delta F$ ($0.999\,999\,483 \pm 63$ for spectrum 6-3/12/83) by comparing the wave numbers of Ar II lines measured in our Fe + Ne + Ar spectrum with the values of Norlén.²⁵ For this comparison we used the 28 standard Ar II lines recommended by Learner and Thorne²⁴ as relatively insensitive to pressure shift.

The uncertainty $\pm \delta F$ in the alignment factor deserves some mention because it makes the largest contribution to the uncertainty in the transition energy, at least for the stronger lines that dominate the least-squares solution because of their greater weight. Although we treat F as a constant, it could depend on the energy of the upper level, because the pressure in Nolen's source was lower than that in ours; we note the effect of source pressure below in this section. Or F could vary with wave number if there is a phase error in our spectrum; Learner and Thorne²⁴ discuss the effect of FTS phase correction on wave number. Because of the possibility that F is dependent on variables that we ignore, we take δF to be the standard deviation of the sample of 28 independent measurements of F . δF is then a measure of our exposure to systematic error arising from the method we use to calibrate the FTS wave-number scale.

However, it should be noted that δF (and indeed the correction factor F itself) may be ignored in the transition energy $\Delta E_{ij} \pm \delta \Delta E_{ij}$ that is input to the least-squares solution and applied only to the results of the calculation, E_i , because the factor F is common to every energy term. Along with the most probable energy values E_i , the CLEVEL code also finds the uncertainty δE_i that is produced by the uncertainty in the observations. δE_i is less than 0.001 cm^{-1} for most levels and is combined with the uncertainty arising from the alignment factor $\delta E_F = (\delta F/F)E_i = (6.3 \times 10^{-8})E_i$ to obtain the total uncertainty $[(\delta E_i)^2 + (\delta E_F)^2]^{1/2}$ assigned to the level energies in Table 3.

Step 5. The level energies E_i that were determined in this least-squares solution were then used to calculate an improved version of the predicted line list, and the sequence of steps 1–4 was repeated to yield the level energies listed in Table 3, refined values for the energy of levels listed in the AEL that satisfy our requirements. The uncertainty in the last digits of the level energy appears in parentheses after the energy value. For comparison we also list the level energies from the 1985 AEL⁵. The level designations follow the recommendations of Brown *et al.*²⁶

A few levels are included in Table 3 even though we see only a single line from the level if (1) the line is expected to be the strongest decay channel within our spectral range on the basis of Kurucz *gf* values⁴ and (2) Brown *et al.*²⁶ confirm the identification of the line in their absorption spectra.

Forty-seven levels in the AEL do not appear in Table 3. Most of the missing levels are $5p$ levels that decay primarily by means of IR transitions outside the 8000–

45 000 cm^{-1} range of spectrum 6-3/12/83. We have seen these IR transitions on other spectra that were used for IR branching-fraction measurements, but, in the interest of presenting a set of level energies based on a single spectrum, in Table 3 we do not include the $5p$ -level energies that can be derived from IR transitions. The following levels were not represented on any of our spectra, even though one expects decay channels within our spectral range: $y^1H_3^o$ (53 722.40), $^5F_2^o$ (53 275.23), $z^1D_2^o$ (49 477.10), $r^3G_{3,4,5}^o$ (60 364, 60 172, 59 926 cm^{-1}). These levels were not seen in the absorption spectra of Brown *et al.*,²⁶ and we doubt their existence.

After we identified 2144 Fe I lines and 161 Fe II lines in spectrum 6, many unidentified lines remained. Some of these are from the neutral and ionized Ar and Ne used in the hollow-cathode source, but there are also Fe lines from unknown Fe I levels. We searched for new levels by adding and subtracting the energy ΔE_u of unclassified transitions to our known energy levels E_i of odd (or even) parity. The set $\{E_i \pm \Delta E_u\}_{iu}$ contains possible values for an unknown even-parity energy level involved in the transition of energy ΔE_u . A cluster of close values in this set, where all partner levels satisfy the δJ selection rule, suggests a possible even- (or odd-) parity level. Additional tests and details of the search procedure are described in Ref. 1. The following levels that do not appear in the 1985 AEL⁵ were identified in this way:

$E = 43\,460.117\text{ cm}^{-1}$, $J = 5$, odd parity; $E = 43\,442.699\text{ cm}^{-1}$, $J = 4$, odd parity. Brown *et al.*²⁶ also saw these levels in absorption and labeled them $z^5I_5^o$ and $z^5I_4^o$, respectively.

$E = 49\,477.124\text{ cm}^{-1}$, $J = 3$, odd parity, probably $S = 0$ because strong transitions are to singlet levels. The AEL lists a level nearby at $49\,477.10\text{ cm}^{-1}$, but its designation $z^1D_2^o$ is wrong. We believe that this level should be labeled $3d^6(a^3F)4s4p(^3P^o)^1F_3^o$ because a singlet F level is expected in this neighborhood, and the level labeled 1F_3 in the AEL at $49\,227.12\text{ cm}^{-1}$ is one of those for which we see no evidence.

$E = 53\,852.110\text{ cm}^{-1}$, $J = 4$, odd parity. We believe that this is the correct J assignment for the level designated $^5G_3^o$ in the AEL at $53\,852.108\text{ cm}^{-1}$.

$E = 24\,574.650\text{ cm}^{-1}$, $J = 4$, even parity, a^1G_4 in the AEL. Many emission lines to this level appear in our spectrum: 8 lines (including the strongest) are from singlet upper levels, 16 are from triplet upper levels, 9 are from quintet levels, and 1 is from a level of unknown spin. The quintet partners would lead us to classify this as a triplet level, but Johansson²⁷ advises that the $\delta S = 2$ transitions reflect spin impurity in the high odd partners. We have not seen $\delta S = 2$ transitions to other levels, but a thorough search with a $\delta S = 2$ predicted line list has not been made.

The level energies in Table 3 are notable in two respects: They have greater precision than any other comprehensive set now available, and they constitute a self-consistent set because all level energies were derived from a single spectrum. A transition energy ΔE , obtained from the difference between level energies in Table 3, is far more precise than either level energy alone, because the systematic uncertainty in ΔE is only $6.3 \times 10^{-8} \Delta E$. However, we em-

Level	Energy (cm ⁻¹)	(±)	NIST Lines
a ⁵ D ₄	0.0000(00)	.000	31
a ⁵ D ₃	415.9333(02)	.932	38
a ⁵ D ₂	704.0061(02)	.004	46
a ⁵ D ₁	888.1313(03)	.129	33
a ⁵ D ₀	978.0730(03)	.072	14
a ⁵ F ₅	6928.2673(05)	.266	47
a ⁵ F ₄	7376.7630(05)	.760	59
a ⁵ F ₃	7728.0584(05)	.056	66
a ⁵ F ₂	7985.7832(06)	.780	62
a ⁵ F ₁	8154.7115(06)	.710	44
a ³ F ₄	11976.2370(08)	.234	41
a ³ F ₃	12560.9325(08)	.930	39
a ³ F ₂	12968.5518(09)	.549	26
a ⁵ P ₃	17550.1783(11)	.175	45
a ⁵ P ₂	17726.9851(11)	.981	55
a ⁵ P ₁	17927.3805(12)	.376	36
a ³ P ₂	18378.1825(12)	.181	38
z ⁷ D ₅	19350.8906(13)	.892	13
a ³ H ₆	19390.1644(13)	.164	24
a ³ P ₁	19552.4752(13)	.473	25
z ⁷ D ₄	19562.4381(13)	.440	19
a ³ H ₅	19621.0050(13)	.005	36
z ⁷ D ₃	19757.0298(13)	.033	16
a ³ H ₄	19788.2482(13)	.245	30
z ⁷ D ₂	19912.4942(13)	.494	15
z ⁷ D ₁	20019.6345(14)	.635	13
a ³ P ₀	20037.8142(15)	.813	9
b ³ F ₄	20641.1079(14)	.109	38
b ³ F ₃	20874.4782(14)	.484	28
b ³ F ₂	21038.9835(14)	.985	19
a ³ G ₅	21715.7303(14)	.730	39
a ³ G ₄	21999.1274(14)	.127	42
a ³ G ₃	22249.4265(15)	.428	35
z ⁷ F ₆	22650.4144(15)	.421	7
b ³ P ₂	22838.3197(15)	.318	33
z ⁷ F ₅	22845.8667(15)	.868	15
b ³ P ₁	22946.8120(15)	.808	31
z ⁷ F ₄	22996.6713(15)	.676	20
b ³ P ₀	23051.7472(16)	.742	11
z ⁷ F ₃	23110.9362(15)	.937	17
z ⁷ F ₂	23192.4960(15)	.497	18
z ⁷ F ₁	23244.8352(15)	.834	11
z ⁷ F ₀	23270.3816(16)	.374	3
z ⁷ P ₀	23711.4536(15)	.457	21
b ³ G ₅	23783.6154(16)	.614	23
b ³ G ₄	24118.8141(16)	.814	31
z ⁷ P ₃	24180.8607(16)	.864	21
c ³ P ₂	24335.7631(16)	.759	29
b ³ G ₃	24338.7626(17)	.762	17
z ⁷ P ₂	24506.9160(16)	.919	14
a ¹ G ₄	24574.6497(16)	.650	33
c ³ P ₁	24772.0147(18)	.017	17
c ³ P ₀	25091.5948(23)	.597	6
z ⁵ D ₄	25899.9860(17)	.987	24
b ³ H ₆	26105.9041(17)	.904	17
z ⁵ D ₃	26140.1762(17)	.177	28
a ³ D ₃	26224.9648(18)	.966	23
z ⁵ D ₂	26339.6933(17)	.691	21
b ³ H ₅	26351.0361(17)	.039	17
a ³ D ₁	26406.4606(20)	.470	9
z ⁵ D ₁	26479.3764(17)	.376	14
z ⁵ D ₀	26550.4748(17)	.476	7
a ³ D ₂	26623.7300(21)	.730	20
b ³ H ₄	26627.6048(18)	.604	18
z ⁵ F ₅	26874.5464(17)	.549	17
z ⁵ F ₄	27166.8170(17)	.819	21
z ⁵ F ₃	27394.6869(17)	.688	21
a ¹ P ₁	27542.9991(21)	.004	10
z ⁵ F ₂	27559.5797(18)	.581	19
z ⁵ F ₁	27666.3441(18)	.346	17
a ¹ D ₂	28604.6070(20)	.606	12
a ¹ H ₅	28819.9513(19)	.946	18

Table 3. Continued

Level	Energy (cm ⁻¹)	(±)	NIST Lines
y S ₂ ⁰	44511.8064(28)	.806	7
w F ₃ ⁵	44551.3333(29)	.330	6
v D ₂ ⁵	44664.0726(29)	.068	5
e D ₄ ⁵	44677.0017(28)	.004	6
v D ₁ ⁵	44760.7409(29)	.75	3
v D ₀ ⁵	44826.8940(30)	.88	1
e D ₃ ⁵	45061.3245(29)	.327	8
x D ₃ ³	45220.6752(29)	.676	8
x D ₂ ³	45281.8273(29)	.831	12
y G ₅ ³	45294.8414(29)	.846	9
e D ₂ ⁵	45333.8716(29)	.874	9
y G ₄ ³	45428.3978(29)	.397	12
e D ₁ ⁵	45509.1481(29)	.150	7
x D ₁ ³	45551.7607(29)	.763	8
y G ₃ ³	45562.9699(29)	.970	11
e D ₀ ⁵	45595.0850(29)	.08	2
x G ₆ ⁵	45608.3581(30)	.31?	2
x G ₅ ⁵	45726.1276(30)	.117	2
x G ₄ ⁵	45833.2181(30)	.20	4
x G ₃ ⁵	45913.4965(30)	.488	3
x G ₂ ⁵	45964.9522(30)	.959	3
z I ₇ ³	45978.0024(30)	.00?	2
z I ₆ ³	46026.9668(30)	.94	3
z I ₅ ³	46135.8123(30)	.88	4
w P ₃ ⁵	46137.0922(30)	.10	3
w P ₂ ⁵	46313.5361(32)	.57	4
w P ₁ ⁵	46410.3780(36)	.40	1
z S ₀ ³	46600.8139(32)	.814	6
y P ₀ ³	46672.5360(33)	.527	3
u D ₄ ⁵	46720.8368(30)	.836	9
y P ₁ ³	46727.0675(30)	.068	9
y D ₂ ⁵	46744.9882(30)	.988	9
u D ₃ ⁵	46888.5124(30)	.510	12
x F ₄ ³	46889.1363(30)	.143	9
y P ₁ ³	46901.8291(30)	.820	10
z H ₀ ³	46982.3149(30)	.34	5
e F ₅ ⁵	47005.5013(30)	.508	8
z H ₁ ³	47008.3655(30)	.366	13
w D ₃ ⁵	47017.1823(30)	.188	9
x F ₃ ³	47092.7060(30)	.707	12
z H ₂ ³	47106.4787(30)	.477	16
w D ₂ ⁵	47136.0792(30)	.072	10
u D ₀ ⁵	47171.5276(31)	.48?	1
u D ₁ ⁵	47177.2302(30)	.225	7
x F ₂ ³	47197.0051(30)	.014	14
w D ₁ ⁵	47272.0229(30)	.016	9
z F ₂ ³	47363.3703(30)	.369	4
e F ₄ ⁵	47377.9491(30)	.962	13
¹ D ₂	47419.6829(31)	.674	9
w G ₅ ⁵	47420.2250(31)	.229	5
z ¹ G ₄	47452.7106(30)	.716	9
y S ₀ ³	47555.6044(31)	.598	9
w G ₄ ⁵	47590.0437(31)	.047	8
v F ₅ ⁵	47606.1118(32)	.094	2
w G ₃ ⁵	47693.2354(31)	.227	7
e F ₃ ⁵	47755.5311(30)	.539	14
x G ₄ ³	47812.1132(31)	.118	12
w G ₂ ⁵	47831.1487(31)	.150	5
x G ₃ ³	47834.2152(32)	.218	7
x G ₅ ³	47834.5456(31)	.542	12
v F ₄ ⁵	47929.9933(31)	.999	6
e F ₄ ³	47960.9366(31)	.941	14
v P ₃ ⁵	47966.5793(31)	.59	2
e F ₂ ⁵	48036.6664(31)	.666	14
v F ₃ ⁵	48122.9249(32)	.928	5
v P ₂ ⁵	48163.4445(36)	.438	5
e F ₁ ⁵	48221.3162(32)	.314	9
y H ₅ ⁵	48231.2742(31)	.270	8
v F ₂ ⁵	48238.8432(31)	.844	13
x P ₂ ³	48304.6376(31)	.638	11
v F ₀ ⁵	48350.6012(32)	.601	3
y H ₄ ⁵	48361.8749(31)	.878	9
z H ₅ ¹	48382.5961(31)	.597	7
x P ₀ ³	48460.1060(33)	.098	5
y H ₃ ⁵	48475.6797(32)	.668	6
x P ₁ ³	48516.1336(32)	.135	14
e F ₃ ³	48531.8621(31)	.864	9
y ¹ G ₄	48702.5291(31)	.526	8
e F ₂ ³	48928.3834(32)	.389	8
w F ₄ ³	49108.8903(31)	.890	9
v D ₃ ⁵	49135.0166(32)	.022	9
v D ₂ ⁵	49242.6149(32)	.593	8
w F ₃ ³	49242.8798(32)	.881	10
v D ₁ ⁵	49297.6282(34)	.620	4
w F ₂ ³	49433.1275(32)	.121	5
y H ₆ ⁵	49434.1569(32)	.156	4
v G ₅ ³	49460.8953(31)	.890	9
¹ F ₃	49477.1226(32)	.10	7
y H ₅ ⁵	49604.4226(32)	.415	6
v G ₄ ³	49627.8787(32)	.877	11
y H ₄ ⁵	49726.9845(32)	.977	8
v G ₃ ³	49850.5847(32)	.581	7
w P ₀ ³	49951.3397(37)	.341	3
w P ₁ ³	50043.2072(34)	.205	8
w P ₂ ³	50186.8283(32)	.830	8
e F ₆ ⁷	50342.1264(32)	.14	3
f D ₅ ⁷	50377.9043(32)	.913	6
f D ₄ ⁵	50423.1330(32)	.136	11
e F ₄ ⁷	50475.2833(32)	.287	7
e G ₆ ⁵	50522.9396(32)	.946	5
f D ₃ ⁵	50534.3900(32)	.391	7
z F ₃ ⁵	50586.8699(33)	.874	6
e F ₃ ⁷	50611.2565(33)	.260	9
x ¹ G ₄	50613.9767(33)	.972	7
e F ₇ ⁷	50651.6290(33)	.72?	1
f D ₂ ⁵	50698.6159(33)	.624	9
e G ₅ ⁵	50703.8651(32)	.866	10
f D ₄ ⁷	50807.9925(32)	.991	8
e F ₅ ⁷	50833.4321(32)	.428	6
e F ₂ ⁷	50861.3238(33)	.321	4
f D ₃ ⁷	50861.8124(35)	.816	6
f D ₁ ⁵	50880.0978(35)	.098	7
e G ₆ ⁷	50967.8260(33)	.826	4
e G ₄ ⁵	50979.5741(33)	.578	8
f D ₀ ⁵	50981.0019(42)	.98	4
f D ₂ ⁷	50998.6408(33)	.641	10
u F ₅ ⁵	51016.6581(40)	.660	1
x H ₃ ⁵	51023.1572(33)	.152	4
f D ₁ ⁷	51048.1002(34)	.113	5
x H ₅ ⁵	51068.7103(33)	.710	9
t D ₄ ⁵	51076.6216(37)	.622	1
f F ₅ ⁵	51103.1870(33)	.187	5
e F ₃ ⁷	51148.8411(44)	.859	2
e S ₂ ⁵	51148.9040(43)	.883	2
e F ₄ ⁷	51192.2686(33)	.270	5
v F ₂ ³	51201.2828(35)	.284	6
e F ₁ ⁷	51207.9943(34)	.991	6
e G ₃ ⁵	51219.0113(33)	.017	9
e G ₅ ⁷	51228.5487(33)	.555	7
e D ₃ ³	51294.2160(33)	.222	6
v F ₄ ³	51304.5994(33)	.603	11
e F ₂ ⁷	51331.0486(34)	.044	6
e G ₄ ⁷	51334.9052(33)	.909	8
g D ₄ ⁵	51350.4883(33)	.491	14
t D ₃ ⁵	51361.3872(55)	.390	4
v F ₃ ³	51365.3046(34)	.308	6
e G ₂ ⁵	51370.1413(34)	.130	6
u G ₅ ³	51373.9040(33)	.909	7
u F ₄ ⁵	51381.4511(32)	.460	3
x H ₄ ³	51409.1209(36)	.117	5
e G ₃ ⁷	51460.5140(33)	.516	6
f F ₄ ⁵	51461.6664(33)	.672	7
e G ₂ ⁷	51539.7171(33)	.712	5
e G ₁ ⁷	51566.7978(34)	.82	3
e S ₃ ⁷	51570.0942(33)	.084	5
f F ₃ ⁵	51604.0999(34)	.102	7
¹ H ₅	51630.1714(34)	.172	8
u G ₄ ⁵	51668.1812(33)	.189	9
f F ₂ ⁵	51705.0108(36)	.007	4
y ¹ D ₂	51708.3018(35)	.309	7
e D ₂ ³	51739.9155(33)	.920	13
f F ₁ ⁵	51754.4933(42)	.490	4
x ¹ D ₀	51762.0726(37)	.067	7
g D ₃ ⁵	51770.5537(34)	.554	14
u G ₃ ³	51825.7689(33)	.773	9
u F ₂ ⁵	51827.4078(50)	.413	1
e P ₃ ⁵	51837.2338(34)	.24	8
u D ₃ ³	51969.0956(34)	.079	5
e P ₁ ⁵	52019.6644(40)	.67	5
e D ₁ ³	52039.8869(34)	.886	4
g D ₂ ⁵	52049.8188(36)	.814	12
e P ₂ ⁵	52067.4642(34)	.460	8
¹ P ₁	52180.8158(36)	.804	4

(continued overleaf)

cathode source and the ICP source (especially with respect to the use of carbonyl and halide vapors of several metals). M. J. Seaton of University College, London, kindly provided unpublished He *gf* values that were used to calibrate the IR response of the FTS. We are indebted to R. L. Kurucz of the Center for Astrophysics for generously supplying millions of semiempirical *gf* values. Finally, we thank S. E. Johansson for valued criticism of our Fe I level energies.

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